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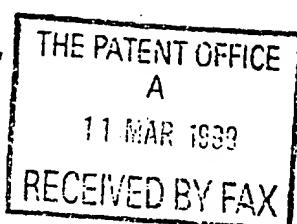
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## Request for grant of a patent

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Newport  
Gwent NP9 1RH

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3 Full name, address and postcode of the applicant	Exxon Chemical Patents Inc. 1900 East Linden Avenue Linden New Jersey 07036 United States of America		
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5 Name of agent Address for service	Harrison Goddard Foote Dr Nicholas J. Whice Whice & Associates Belmont House Windsor House 20 Wood Lane Cornwall Road Huddinge HA6 6GATE Leeds LS6 2AE NG1 2PW		
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7	Parent application (eg Divisional)	Earlier Application No	Date of Filing
8	Statement of Inventorship Needed?	YES	
9	Number of sheets for any of the following (not counting copies of same document)		
Continuation sheets of this form			
	Description	31 ✓	
	Claims	2 ✓	
	Abstract	1 ✓	
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10	Number of other documents attached		
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Processes for The Manufacture of Supported Materials

This invention relates to a method for the preparation of supported inorganic layers.

5 Inorganic materials find extensive use as catalysts and membranes. In a number of applications it is desirable and sometimes essential that the inorganic material is used in conjunction with a physical support structure. The support structure may be required to ensure adequate mechanical strength of the inorganic material when for example it is in the form of a layer. In other applications it enables the easy 10 application and removal of the inorganic material from, for example, a catalyst bed.

There are numerous methods described in the art for the manufacture of support materials for inorganic catalysts and membranes. There is however a continual need for improved methods of support preparation and manufacture of supported inorganic 15 layers.

When supports are used in the manufacture of inorganic layers they may suffer a number of problems which are dependant, inter alia, on the techniques used for manufacturing the inorganic layer. When the inorganic layer is a molecular sieve 20 layer which has been manufactured using hydrothermal synthesis techniques a number of problems may arise. Firstly, unwanted material may be deposited within the support structure resulting in unwanted catalytic sites and/or reduction in porosity of the support. Secondly, the support material may not be inert under the synthesis conditions used; this may result in the support dissolving to an unacceptably 25 significant extent and/or the incorporation of unwanted material from the support into the inorganic layer. Thirdly, after deposition of the inorganic layer the complete structure may lack acceptable mechanical integrity resulting in cracking and/or delamination problems.

30 Gavalas et.al describe the use of a specific barrier in zeolite membrane synthesis; "Use of diffusion barriers in the preparation of supported zeolite ZSM-5

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membranes", Journal of Membrane Science, 126 (1997), 53-65. In their method a mixture of furfuryl alcohol and tetraethylorthosilicate (TEOS) is impregnated into a support, after which the mixture is polymerised by exposure to p-toluene sulfonic acid at elevated temperature and the resulting polymer is carbonized. After 5 deposition of the zeolite membrane the carbon is removed under calcination conditions, however the TEOS is converted to a silicate which is deposited within and remains in the pores of the support. Prior to deposition of the zeolite layer the carbonised polymer is selectively and deliberately removed from the top region of the support.

10

The support structure manufactured according to the present invention overcomes some or all of the problems identified above depending on the properties of the support used and the method of manufacture of the inorganic layer. The resultant support structure provides improved control during subsequent deposition processes 15 which may be used for the manufacture of inorganic material layers. The support structures prepared by the process of the present invention, enable control over where the inorganic material is to be deposited and/or assist in maintaining the integrity of the combined support and layer structure. They also assist in ensuring reproducible manufacture of the inorganic layer and assist in overcoming problems associated 20 with dissolution of the support.

In a specific embodiment the method of the present invention provides molecular sieve layers which have good properties compared to molecular sieve layers in the art for both catalytic and/or membrane applications.

25

The present invention therefore provides in a first aspect a process for the manufacture of a supported inorganic layer, which process comprises:

30 a) providing a porous inorganic support which has at least one surface capable of receiving an inorganic layer,

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5                   b) impregnating the porous inorganic support through at least one surface thereof with a material capable of removal from the support after receipt of the inorganic layer and which material is not carbonised prior to receipt of the inorganic layer,

10                   c) depositing or growing an inorganic layer on the surface mentioned in (a);  
                      and

15                   d) substantially completely removing the impregnating material.

As examples of porous supports, there may be mentioned porous glass, sintered porous metals, e.g., steel such as stainless steel or nickel, an inorganic oxide, e.g., alpha-alumina, titania, cordierite, zeolite as herein defined or zirconia and mixtures 15 of any of these materials. In this context porous supports include supports which have pores which are occluded; such supports whilst having pores are not generally suitable for membrane separation applications but may be used for catalytic applications or separation processes which are not membrane separation processes.

20                   The pore size and porosity of the support should be compatible with the process employed for manufacturing the inorganic layer. The support may be any material compatible with the coating and synthesis techniques utilised in the process of the present invention. For example porous alpha-alumina with a surface pore size within the range of 0.08 to 1  $\mu$ m, most preferably from 0.08 to 0.16  $\mu$ m, and advantageously 25 with a narrow pore size distribution. Ideally the support should have a relatively high degree of porosity so that the support has an insignificant effect on flux through the finished product. Preferably the porosity of the support is 30% by volume or greater. The support may be multilayered; for example, to improve the mass transfer characteristics of the support, only the surface region of the support in contact with 30 the inorganic layer may have small diameter pores, while the bulk of the support, toward the surface remote from the inorganic layer, may have large diameter pores.

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An example of such a multilayered support is an alpha-alumina disk having pores of about 1  $\mu$ m diameter coated with a layer of alpha-alumina with pore size about 0.1  $\mu$ m. A further example of a multilayered support is a large pore metal based support which has an inorganic layer deposited thereon of smaller pore size compared to the metal support. It is to be understood, that when the support is a molecular sieve, as herein defined, and at least at its surface it has the requisite properties to function as a seed layer, as described below in relation to particle size and crystallinity, then the ~~support surface itself may act as the seed layer and a deposited seed layer, as~~ described below, may be dispensed with. Zeolite supports may however also be used in conjunction with a deposited molecular sieve seed layer. Suitable supports include the composite membranes and layers manufactured according to US 4 981 590 and US 5 089 299.

At least one surface of the support is capable of receiving the inorganic layer or when used a seed layer. The preparation of this surface will depend on the quality, chemical or physical properties of the support when considered in combination with the desired method of deposition of the inorganic layer or, when used, the seed layer.

Thus some support materials will require chemical or mechanical treatment to ensure that they are chemically and/or physically compatible with the inorganic layer. For example, rigorous cleaning of the support surface may be required to remove undesirable surface contamination. Physical abrasion may be used to provide a smooth support surface for deposition. In one form of preparation prior to impregnation a seed layer may be deposited for use in seeded molecular sieve growth.

It is preferred that the support is such that it is substantially inert under the reaction conditions used for deposition of the inorganic layer and that no chemical component of the support participates in the molecular sieve synthesis.

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The support may be cleaned prior to deposition of the inorganic layer or seed layer as described below. Suitable cleaning techniques include ultrasonic treatment in water, pentane, acetone or methanol. This may be followed by a period of drying from a few minutes to 24 hours under ambient conditions or under temperatures up to

5 1000°C, preferably 500 to 700°C. The cleaning regime may comprise a combination of cleaning steps. Such a combination may be a series of washing steps with different solvents and/or drying steps. Each solvent washing step may be utilised in

~~combination with ultrasound.~~

- 10 The impregnating material may be any material which substantially remains within the support during the subsequent process used for deposition of the inorganic layer e.g. hydrothermal synthesis, and which is substantially stable under the deposition conditions used, at least for the period of the deposition process.
- 15 The impregnation material selected must remain within the support, and must remain stable, under the deposition conditions so as not to interfere with the deposition process and to ensure that an inorganic layer of the desired quality and properties is obtained in the process.
- 20 Ideally the impregnation material should have a viscosity which enables easy impregnation into the support. The properties of the material ideally are such that it may be impregnated into the support under capillary action, applied pressure or a vacuum. Furthermore the impregnation material should be compatible with the physical properties of the support surfaces to ensure that it can wet the surfaces of the support and intimately contact with it.
- 25

The impregnation material should also be capable of being easily and substantially completely removed from the support after formation of the inorganic layer. Ideally at least the bulk of the impregnating material is capable of being removed under an

- 30 applied pressure, by washing of the support with a suitable solvent, via calcination, via melting or any combination of these methods. It is preferred that the

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impregnation material is capable of being removed under calcination conditions which are normally used in the manufacture of molecular sieve materials such as those used in zeolite synthesis. It is important that the impregnation material can easily be removed in order to ensure that no residual material remains which could 5 impair the performance of the inorganic layer.

The preferred impregnation materials include natural or synthetic organic resins e.g. hydrocarbon resins. In the context of the present invention hydrocarbon means an organic material which has as its main components hydrogen and carbon but does not 10 preclude the presence of one or more heteroatomic species e.g. oxygen or nitrogen or chlorine. One preferred class of impregnating materials, are the hydrocarbon resins free of heteroatoms. If a heteroatom is present it is preferred that it is oxygen or chlorine. Examples of suitable resins are acrylic resins, PVC resins, hydrocarbon waxes, ethylene-butene copolymers and polyisobutylenes.

15 Examples of suitable acrylic resins are the L R White Resins of the London Resin Co. These are hydrophilic acrylic resins of low viscosity (typically 8cps) which are commercially available in three grades of hardness; LR1280 hard grade, LR1281 medium grade and LR1282 soft grade. These resins may be thermally or cold cured, 20 with or without the use of an accelerator (LR1283).

25 Examples of suitable hydrocarbon resins are the hydrocarbon waxes such as Exxon ESCOMER™ H101 and H231. H101 has a molecular weight within the range 1600 to 2300 and a viscosity at 121°C of 25.5 cps, at 140°C of 17 cps and at 190°C of 9 cps. H231 has an approximate molecular weight of 6590 and a viscosity at 121°C of 600 mPas.

30 An example of a suitable impregnating material incorporating PVC is a PVC plastisol. Such plastisols are well known in the art and typically comprise PVC in combination with plasticizer, stabiliser and viscosity depressor.

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A further example of suitable impregnating materials are ethylene-butylene resins of molecular weight 300 to 10000 or polyisobutylenes of molecular weight 500 to 5000.

When a seed layer is used it may be deposited prior to or after impregnation; 5 preferably it is deposited prior to the impregnation of the support. In this instance after impregnation of the support there may be quantities of impregnating material located on the surface of the seed layer which is deposited on the support. If this deposited layer of impregnating material is relatively thin or discontinuous then surprisingly it may not have an adverse effect on the seeding properties of the seed 10 layer and need not be removed. This is especially the case where the impregnating material is mildly unstable under the deposition conditions e.g hydrothermal synthesis conditions, and is slowly dissolved in the synthesis mixture. Such a material has acceptable stability. Examples of materials which have this property include, the hydrocarbon waxes, acrylic resins and ethylene/butene resins described 15 above. If necessary it may be removed from the surface of the seed layer by any suitable means. One suitable means, in the case where a co-solvent is used for impregnation, is to use the same solvent to clean the surface of the seed layer. When no co-solvent is used then any suitable solvent for the resin may be used to clean the seed layer surface. The thickness of this surface deposited layer should be less than 1 20 um and preferably should be less than 0.5 um, most preferably less than 0.1 um

The most preferred resins are the hydrocarbon wax resins which may easily impregnate the support and which are removed from the support under calcination temperatures normally used in zeolite synthesis, with or without prior melting of the 25 bulk material.

Materials such as some low molecular weight hydrocarbons e.g hexadecane, silicone oils and polyimide resins have been found to be unsuitable as impregnating materials. This is mainly due to their propensity for relatively rapid removal from 30 the support under deposition conditions.

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The resins may be used alone or in combination with each other and/or other materials which may be required to assist in their impregnation. For example the PVC resins may advantageously be impregnated into the support as a solution in THF; the THF being evaporated prior to deposition of the inorganic layer. Other 5 suitable solvents may be used in conjunction with the resins. The resins may be applied in the molten form under ambient pressure conditions or under an applied pressure; for example hydrocarbon waxes are advantageously applied in the molten form.

10 The impregnation stage may be repeated one or more times to ensure that the pores of the support, which are at or proximate to the surface for deposition of the inorganic layer, are substantially filled with impregnating material.

15 In one embodiment the support is impregnated through surfaces of the support other than the surface capable of receiving an inorganic layer. For example a support in the form of a disk may have one side capable of receiving an inorganic layer. The other side of the disk may be impregnated. In one embodiment, the impregnation may be partial so as to fill the pores of the surfaces other than the surface capable of receiving an inorganic layer. This partial filling of the pores is acceptable if it results 20 in improved performance of the inorganic layer compared to that manufactured without impregnation. Partial impregnation is particularly suitable when a seed layer is used and the inorganic layer is deposited via hydrothermal synthesis from a synthesis solution which comprises colloidal silica. Surprisingly the combination of seed layer and colloidal silica in the synthesis solution allows the use of partial 25 impregnation. Impregnation may be continued until substantially all the pores of the support are impregnated including pores proximate to the surface capable of receiving the inorganic layer. In the case of wax impregnation this may be observed visually by an optical change in the support and degree of impregnation can be confirmed by cross-section SEM. In a further embodiment the support may be 30 impregnated through the surface capable of receiving an inorganic layer.

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After impregnation the nature of the organic resin may be such that it is advantageous to cure the resin in-situ prior to use in the manufacture of an active inorganic material. This curing ensures that the resin remains in the impregnated location. It is preferred that the impregnating material has a melting point at or 5 above the temperature used in the process for deposition of the inorganic layer.

The inorganic material may be deposited on the surface capable of receiving the material as individual particles which are substantially located within the same plane after deposition, or in the form of a contiguous layer of particles where there is 10 contact of substantially all particles with at least one of its neighbours. It may also be deposited in the form of a continuous film of material. Any inorganic material may be used in the process of the present invention. Methods of their deposition are well known in the art. Examples of suitable inorganic materials include catalysts either in the particulate form or as a layer, alone or in combination with other materials such 15 as intercalating compounds and binders. The methods for the manufacture of supported catalysts are well known in the art and such methods as they relate to deposition of the active catalyst material on the support may be utilised in the present invention. Another example of an inorganic layer is an inorganic membrane.

20 A particularly preferred inorganic layer for use in the present invention is one based on molecular sieve materials, such as zeolite materials, either in the form of catalysts or in the form of membrane layers. The inorganic material may, for example, be a seed layer precursor to a molecular sieve membrane as described below. It may be a molecular sieve membrane layer alone or in combination with such a seed layer.

25 The porous inorganic support may comprise a seed layer and the impregnating material may be impregnated into the seed layer only or into the seed layer and the base support material.

30 When the inorganic layer is a molecular sieve layer it may be manufactured using techniques which are well known in the art. For example suitable methods of

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manufacture of molecular sieve layers are described in US 5 110 478, US 5 100 596, US 5 019 263, US 5 069 794, EP 0 481 658, EP, 0 481 659, EP 0 481 660, EP 0 632 743, NL9100217, NL9101126, NL9101148, NL 9201204 and WO 94/25151. The disclosures of which in so far as they relate to deposition of molecular sieve layers  
5 are incorporated by reference.

The preferred method for the manufacture of the molecular sieve layer is a seeded hydrothermal synthesis process. The supports of the present invention are particularly useful in such processes for the manufacture of molecular sieve layers.  
10 These methods are described in WO 96/01683, WO 96/01685, WO 96/01686, WO 96/01687 and PCT/EP97/01267.

In this method the seed layer comprises molecular sieve crystals of average particle size 200 nm or less. Advantageously, the crystal size of the molecular sieve in the  
15 seed layer is 100 nm or less ideally within the range 5 to 100 nm and most preferably within the range 25 to 75 nm.

The seed layer advantageously consists essentially of the molecular sieve material, or may be a composite of the molecular sieve material and intercalating material. The  
20 particles of the seed layer may be contiguous or non-contiguous; preferably they are contiguous. The intercalating material may be the same material as the support.

The colloidal molecular sieve seed crystals may be prepared by processes which are well known in the art, such as those described in International Applications  
25 WO93/08125, WO97/03019 WO97/03020 WO97/03021 and WO94/05597, the disclosures of which in so far as they refer to the manufacture of colloidal seeds and their use in the manufacture of layers, are incorporated by reference.

The seed layer may be applied to the support by techniques known in the art, for  
30 example, spin-coating, wash-coating, spray-coating, brushing, slip-casting or dip-coating in a suspension of the colloidal molecular sieve crystals.

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The colloidal crystals are preferably applied to the support by spin-coating, the viscosity of the mixture, solids concentration and the spin rate inter alia controlling the coating thickness. The mixture may firstly be contacted with the stationary support, then after a short contact time the support is spun at the desired rate. Alternatively the mixture is contacted with a support which is already spinning at the desired rate.

The thickness of the seed layer is preferably 2 $\mu$ m or less, most preferably at most 10  $\mu$ m or 0.5  $\mu$ m or less. Advantageously, the seed layer is of sufficient thickness to cover irregularities of comparable scale in the surface of the support. Advantageously, the seed layer is at most the thickness of the subsequently deposited molecular sieve layer.

15 In one embodiment the seed layer may be deposited and used as a monolayer. Such a monolayer and its method of deposition is described in WO97/33684, the disclosure of which in so far as it relates to the manufacture of a seed monolayer is incorporated by reference.

20 In one aspect of the process of the present invention the support may be impregnated and placed into the molecular sieve synthesis mixture without any further treatment of the seed layer after its deposition. Even when submerged in the synthesis mixture, the particles in the seed layer remain adhered to the support and facilitate growth of the zeolitic layer. However, under some circumstances, 25 e.g. during stirring or agitation of the synthesis mixture, the adhesion between the particles and the support may be insufficient and steps must be taken to stabilise the seed layer.

30 Therefore, in another aspect of the invention, the seed layer is stabilised before being placed into the synthesis mixture. This stabilisation can be achieved in one aspect by heat-treating the seed layer, e.g. at temperatures between 30 and 1000°C, ideally

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greater than 50°C and more preferably between 200°C and 1000°C and most preferably greater than 300°C and between 400°C and 600°C for several hours preferably at least two hours most preferably 2 to 10 hours.

5 In a further embodiment the seed layer molecular sieve crystals are synthesized in situ on the support before the upper layer is applied by hydrothermal treatment of a synthesis mixture in the presence of the support. In this embodiment the support is impregnated as described above, prior to deposition of the seed layer. According to

10 this embodiment, the process comprises preparing a first synthesis mixture comprising a source of silica and an organic structure directing agent in a proportion sufficient to effect substantially complete dissolution of the silica source in the mixture at the boiling temperature of the mixture, contacting the support in the synthesis mixture, crystallizing zeolite from the synthesis mixture onto the support, to form the seed layer. This procedure may be carried out as described in the above-mentioned Application WO 94/25151. The resulting coated support is then immersed

15 in a second synthesis mixture and subjected to hydrothermal treatment.

20 The composition of the synthesis solution is selected to provide the desired molecular sieve or molecular sieve type and such appropriate synthesis solution compositions are provided in the above identified prior art references. When the molecular sieve layer comprises silica in its framework then the H<sub>2</sub>O to SiO<sub>2</sub> ratio ideally is within the range of 7 to 60. In a preferred embodiment the silicon source comprises colloidal silica. Preferably the H<sub>2</sub>O to SiO<sub>2</sub> ratio is within the range of 7 to 30 and most preferably within the range 7 to 20. For certain molecular sieves such as

25 aluminophosphates a source of silica is not required.

30 The composition of the synthesis mixture varies according to the process; the mixture always contains sources of the various components of the desired molecular sieves and usually contains a structure directing agent. A preferred colloidal silica source is an ammonia-stabilised colloidal silica, e.g., that available from du Pont under the trade mark Ludox AS-40. The use of colloidal silica is preferred when the support is

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partially impregnated and a seed layer is deposited on the surface capable of receiving the inorganic layer.

The source of silicon may also be the source of potassium, in the form of potassium silicate. Such a silicate is conveniently in the form of an aqueous solution such, for example, as sold by Aremco Products, Inc. under the trade mark CERAMA-BIND, which is available as a solution of pH 11.3, specific gravity 1.26, and viscosity 40 mPas. Other sources of silicon include, for example, silicic acid.

10 As other sources of potassium, when present, there may be mentioned the hydroxide. Whether or not the synthesis mixture contains a potassium source, it may also contain sodium hydroxide to give the desired alkalinity.

15 The structure directing agent, when present, may be any of those commonly used in zeolite synthesis. For the manufacture of an MFI layer, a tetrapropylammonium hydroxide or halide is advantageously used.

20 For the manufacture of an MFI type zeolite, especially ZSM-5 or silicalite-1, the synthesis mixture is advantageously of a molar composition, calculated in terms of oxides, within the ranges:

$M_2O:SiO_2$	0 to 0.7 to 1 preferably 0.016 to 0.350:1
$SiO_2:Al_2O_3$	12 to infinity :1
$(TPA)_2O:SiO_2$	0 to 0.2:1 preferably 0 to 0.075 :1
25 $H_2O:SiO_2$	7 to 60:1 preferably 9 to 30 :1

wherein TPA represents tetrapropylammonium and M an alkali metal, preferably sodium or potassium, but also Li, Cs and also ammonia. Other template agents may be used in these ratios.

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In this specification ratios with infinity as the value indicate that one of the ratio materials is not present in the mixture.

5 In a preferred aspect the process of the present invention utilises a hydrothermal synthesis temperature of 140°C or less, preferably within the range from 60 to 100 °C, and most preferably within the range 60 to 90°C. It is preferred that the hydrothermal synthesis temperature is at or below the melting point of the impregnating material.

10 In a preferred aspect the process of the present invention utilises a synthesis time of 1 to 200 hours, preferably 4 to 100 hours, in particular 4 to 80 hours and most preferably 4 to 36 hours.

15 The hydrothermal treatment advantageously is undertaken in an autoclave under autogenous pressure. However with synthesis temperatures below 100°C it is possible to undertake the synthesis under ambient pressure conditions.

20 After deposition of the molecular sieve layer the impregnating material is substantially removed by any of the methods or combination of methods indicated above. The removal method chosen will depend to some extent on the exact nature of the impregnating material. The essential requirement is that the removal method is capable of removing substantially all of the impregnated material. One suitable method is to utilise the final calcination step in the molecular sieve synthesis process to remove the impregnating material.

25 After crystallisation, the structure may be washed, dried, and the molecular sieve calcined. The calcination conditions preferably comprise slow heating and cooling to ensure that the structure, and in particular the molecular sieve layer, remains intact. Preferably the structure is calcined at a temperature of 350 to 600°C, preferably 450 to 550°C. It is preferred that the structure is raised to the desired calcination temperature at a rate of 0.1 to 6°C per minute most preferably 0.2 to 3°C per minute.

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In relation to the processes described herein contacting is to be understood to include immersion or partial immersion of the substrate in the relevant zeolite synthesis mixture.

5

The molecular sieve layer may be any known molecular sieve material; for example it may be a silicate, an aluminosilicate, an aluminophosphate, a silicoaluminophosphate, a metalloaluminophosphate, or a metalloaluminophosphosilicate.

10

The preferred molecular sieve will depend on the chosen application, e.g. separation, catalytic applications, and combined reaction and separation, and on the size of the molecules being treated. There are many known ways to tailor the properties of the molecular sieves, for example, structure type, chemical composition, ion-exchange, and activation procedures.

15

Representative examples are molecular sieves/zeolites which may be used in the molecular sieve layer include the structure types AFI, AEL, BEA, CHA, EUO, FAU, FER, KFI, LTA, LTL, MAZ, MOR, MEL, MTW, OFF, TON and, especially, MFI.

20

The structure types of the seed and molecular sieve layers may be the same or different. Further, if the structure types are the same, the compositions may be the same or different.

25

Some of the above materials while not being true zeolites are frequently referred to in the literature as such, and this term will be used broadly in this specification.

30

The process of the present invention provides molecular sieve layers with good separation properties. Molecular sieve layers, especially when in the form of a membrane, have been characterised by means of a number of analytical techniques. One such technique is the dye permeation test as described in WO96/01683. Whilst

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this test is a good indication as to whether or not unacceptable defects are present in a molecular sieve layer, it is a coarse test and filter, and does not provide any absolute measurable difference which is quantifiable between different molecular sieve layers which pass the test. Molecular sieve layers have been further characterised using x-ray diffraction, transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Such techniques have been used to characterise molecular sieve membranes in for example WO96/01683. In the context of the present invention these techniques may be used to observe the degree of invasion of the inorganic layer into the support after deposition; however although useful information this is still a qualitative measure of success. Using these techniques it may be seen that supported layers of the present invention are not significantly invaded with deposits of material which constitutes the inorganic layer or other inorganic species. It has been observed that if the layers of the present invention are evaluated for their helium permeance, then they are found to have improved permeances compared to layers not manufactured according to the present invention. Furthermore their paraxylene selectivity and permeance may also be improved.

The molecular sieve layers of the present invention may be treated to further improve or stabilise their properties. In one aspect, whilst intact layer regions are of good quality, there may be regions of the layer which are cracked or where there may be pinholes present. If these cracks and pinholes are of such quantity and dimensions that they have a disproportionate effect on membrane performance then it is useful to reparate the layer. Suitable reparation techniques are described in for example WO96/01682, WO96/01686 and WO97/25129, the disclosures of which are incorporated by reference. The preferred method of reparation is that described in WO96/01686. If the molecular sieve layer of the present invention has no pinholes or cracks which disproportionately effect the layer performance it may still be advantageous to treat the molecular sieve layer to maintain its performance. In this context a suitable treatment is the selectivity enhancing layers described in WO96/01686. Such selectivity enhancing layers may at the same time also reparate defective molecular sieve layers.

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The process of the present invention provides active inorganic layers with good properties. When the active inorganic material is a catalyst it enables the porosity of the support to be maintained to facilitate access of the reactants to the catalyst surface. When the active inorganic material is a membrane it allows the porosity of the support to be maintained to ensure that it does not exhibit resistance to the flow of material through the membrane. When used for the manufacture of molecular sieve membranes the process of the present invention provides membranes which have the enhanced combination of selectivity and permeance, even for relatively thin membranes of less than 1 um.

The thickness of the molecular sieve layer is advantageously less than 2  $\mu$ m ideally within the range of 0.1 to 2  $\mu$ m, more advantageously from 0.1 to 1  $\mu$ m, and preferably from 0.1 to 0.5  $\mu$ m. Advantageously, the thickness of the layer and the crystallite size of the molecular sieve are such that the layer thickness is approximately the size of the longest edges of the crystals, giving essentially a monolayer. Advantageously the crystals of the molecular sieve layer exhibit a columnar Shape Preferred Orientation.

The layers may be configured as a membrane, a term used herein to describe a barrier having separation properties, for separation of fluid (gaseous, liquid, or mixed) mixtures, for example, separation of a feed for a reaction from a feedstock mixture, or in catalytic applications, which may if desired combine catalysed conversion of a reactant or reactants and separation of reaction products.

25

The following Examples, in which parts are by weight unless indicated otherwise, illustrate the invention:

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ExamplesA. Impregnation Methods5 Method 1

A one inch alumina disk with a seed layer deposited on one surface was placed with the non-deposited surface face down on a filter paper that had been soaked with an acrylic resin. The disk was left in place until the resin had diffused through the non-deposited surface and upto the top surface of the deposited layer. Completion of this impregnation was detected optically by a change in the appearance of the top surface of the disk.

15 The impregnated disk was then removed from the resin and the excess resin present on the no-deposited surface was removed with a low lint paper wipe. An accelerator was applied to the non-deposited surface of the disk and it was allowed to diffuse into the acrylic resin in the disk for a period of five minutes after which the excess accelerator was wiped from the disk. The acrylic resin was then cured by exposure through the deposited surface of the disk to UV light for greater than eight hours.

20 After curing the impregnated support was ready for deposition of an inorganic layer.

Method 2

25 In this method a mixture of acrylic resin and accelerator are impregnated through the surface with the deposited seed layer and acrylic resin in the impregnated support is cured in the same way.

Method 3

30  $\alpha$ -alumina supports having a porosity of about 33% and pores of approximately 80 to 100 nm, were cleaned and then a seed layer was deposited on one surface.

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A petri dish was partially filled with H101 hydrocarbon wax which was melted at 150°C in a vacuum oven. The coated support was placed on a holder in the wax filled petri dish such that only the non-deposited surface of the support was 5 submerged in the wax. This ensured that the seed layer did not come into direct contact with the wax. The vacuum pump was switched on and after 2 minutes it was switched off at a vacuum of <50mbar. The oven was brought to atmospheric pressure and the impregnated wax was allowed to solidify within the pores of the  
support. This impregnated support was now ready for deposition of an inorganic 10 layer.

Example 1 and Comparative Example 1

In these examples the supported layers were manufactured as follows

15 Support Pretreatment

Two polished  $\alpha$ -alumina disks having a porosity of about 33% and pores of approximately 80 to 100nm, were cleaned ultrasonically in pentane and acetone.

20 Seed Coating

The disks were spin coated with a colloidal suspension of approximately 50 nm colloidal silicalite seeds at 0.25 wt% solids, for 30 seconds at 4000 rpm. Then the 25 disks were heat treated at 350 °C for 6 hours (heat up rate 0.3°C/min).

Impregnation

One of the disks was impregnated with LR White Acrylic Resin (Hard Grade, 30 London Resin Company) under vacuum. The disks were covered with xylene, which was spun off after 20 seconds (4000 rpm/30 secs). The resin was cured overnight at

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70°C in a N<sub>2</sub>-atmosphere. This whole process was repeated once in order to fill any pores that may have opened up through withdrawal of the acrylic.

Deposition of Molecular Sieve Layer

5

The impregnated and non-impregnated disks were placed, seeded side facing downwards, in teflon-lined autoclaves. The disks were ca. 9 mm above the autoclave floor. ~~The synthesis mixture, with molar composition 10 SiO<sub>2</sub> / 0.81 TPABr / 0.13~~

Na<sub>2</sub>O / 2.60 K<sub>2</sub>O / 750 H<sub>2</sub>O was poured into the autoclaves, fully covering the disks.

10 The autoclaves were closed, heated up to 140°C in 30 minutes and kept at 140°C for 4 hours. The disks were taken out of the autoclaves, washed, dried, and calcined for 6 hours at 500°C. Under these conditions the LR Acrylic resin was removed completely from the impregnated disk.

15 Air permeation test

The air permeation of the two samples was tested prior to reparation and the results are provided in Table 1. It is clear that the structure exhibits a higher air permeation after calcination than the molecular sieve layer on a support without resin

20 impregnation; this suggests a more open structure of the support.

Table 1: Inorganic Layer Performance

Disk no.	Air permeation** ml/min	P <sub>XY</sub> /m <sub>X</sub> selectivity*	P <sub>XY</sub> permeance* Kg/m <sup>2</sup> .day.atm <sub>P<sub>XY</sub></sub>
Example 1	10.9	13.6	5.3
Comparative Example 1	3.3	5.5	4.5

\*1 bara,  $\Delta P=0$ , 360°C

\*\*RT,  $\Delta P=2$  bar

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Membrane reparation

The disks were placed on the vacuum chuck of a Convac MTS-4 spincoater, covered  
5 with Hitachi PJX8144 polyimide, and spun at 6500 rpm for 30 seconds. The  
polyimide was cured to a maximum temperature of 325°C. These reparation layers  
were then tested for their xylenes separation performance.

---

Xylenes Separation Test

10

A simplified diagram of a unit used to test the supported molecular sieve layers is  
shown in Figure 1. Feed, preheated and vaporized inside a sandbath, and sweep flow  
into stainless steel cell containing a membrane. This cell is designed such that select  
feed components pass through the membrane from the feed side to the sweep side at  
15 process conditions. Product streams labelled retentate (feed depleted of select  
components) and permeate (sweep enriched with select components) separately, but  
simultaneously, flow out of the membrane cell. The permeate is analysed by an on-  
line chromatograph (GC), and the composition of the permeate is used in conjunction  
with the permeate flow to calculate the flow of each individual component through  
20 the membrane.

Following is a detailed description of the testing procedure.

1. The membrane is mounted into a metal (steel) cell and sealed with a graphoil  
25 o-ring. It is preferable to have the surface of the steel cell passivated so that it  
does not induce catalytic cracking and coking reactions in the test. The  
catalytic activity of the cell and membrane assembly can be assessed by  
measuring the level of cracking products in the permeate. It is also preferable  
30 to pretreat the graphoil o-ring so that it does not outgass carbonaceous  
materials which have the potential of fouling the membrane and reducing  
observed xylenes flows through the membrane. One procedure for

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pretreating graphoil o-rings is heating up under air at 450°C for 3 h and the cool down them down to room temperature. It should be noted that the graphoil o-ring is applied directly to the zeolite layer.

5 2. The cell with membrane mounted inside is then heated to the temperature at which the test is to be performed. A heating rate which has been used in many of the tests is ~2°C/min. While the membrane is being heated, ~~hydrogen is flowed across the feed and sweep side of the membrane. Flow~~

10 rates for tests with a ~2.5cm diameter membrane sealed with a graphoil gasket which exposes an area of 2.9 cm<sup>2</sup> to the feed are:

Example	ml/min at 1 bar absolute on the feed side	ml/min at 1 bar absolute on the sweep side
1 to 3	20	10
4 to 12	100	100

15 It should be noted that the feed side is the side of the membrane structure sealed by the graphoil gasket (i.e., the side on which the zeolite layer is deposited).

20 For the ~2.5 cm diameter membrane, a liquid hydrocarbon mixture which is primarily composed of xylene isomers is introduced at a rate of 4 ml/h for examples 1 to 3 and 33 ml/h for examples 4 to 12, into the hydrogen flowing on the feed side of the membrane. The line carrying the mixture to the cell passes through enough of a hot zone to vaporize the feed and to bring the mixture to the temperature at which the test is to be conducted. The pressure on the feed side is then increased to 2 bar absolute for examples 4 to 12 and 1 bar absolute for examples 1 to 3. At the testing temperatures, the hydrogen partial pressure on the feed side is approximately equal to the hydrogen partial pressure in the flowing hydrogen sweep stream. With this testing

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procedure, hydrogen transference through the membrane is minimized, simplifying interpretation of results.

5 The composition of the hydrocarbon mixture used in the examples provided is nominally 70% metaxylene (mX), 20% paraxylene (pX), 5% ethylbenzene (EB), and 5% trimethyl-benzene (TMB) by weight for examples 4 to 12 and 10 50% metaxylene (mX), 20% paraxylene (pX), 15% orthoxylene (oX), and 15% ethylbenzene (EB) by volume for examples 1 to 3. It is preferable that the oxygen level in these mixtures be low to prevent chemical reactions which can lead to coking. This can be done by degassing the mixtures, and by formulating the mixtures from oxygen free solvents.

15 4. The composition of the hydrocarbons in the permeate stream is measured with an FID detector in a gas chromatograph. The integrated area for each component is used to deduce the flux of each component, the integrated area can be related to the mass fraction of a component in the permeate by a calibration procedure in which a known concentration of mixture components is passed through the gas chromatograph. The values selected for characterising the membrane were taken after the test unit had been exposed 20 to the hydrocarbon mixture for 6 hours (i.e. on oil for 6 hours). For reparation membranes the test is undertaken for 1.5 hours.

25 5. Hydrogen flow rates are measured in permeate and retentate.

$$\text{Permeance of A} = \frac{\text{Mass Flow Rate of A in Permeate}}{(\text{Partial Pressure of A in Feed} - \text{Partial Pressure of A in Sweep}) * \text{Area}}$$

30 Area = Membrane area exposed to feed by graphoil gasket

Permeance is expressed as  $\text{Kg}_A/\text{m}^2 \cdot \text{day} \cdot \text{atm}_A$

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Under certain circumstances, the transfer of hydrocarbons through the membrane from feed to sweep is low enough that the partial pressure of hydrocarbons in the sweep is negligible (note that hydrocarbons are not added to the sweep so any hydrocarbons present in the permeate must flow through the membrane). In such 5 circumstances, one may opt to neglect the partial pressure of hydrocarbon A in the sweep and calculate the permeance of A using the partial pressure of hydrocarbon A in the feed as the total transmembrane pressure driving force. The error in such approximation is equal to the ratio of the partial pressure of A in the sweep to the partial pressure of A in the feed. Thus, it follows that if the partial pressure of A in 10 the sweep is much lower than the partial pressure of A in the feed, the error is low. Using the flow rates given here to test the membranes described in this invention, the partial pressure of each hydrocarbon in the sweep is less than five percent of the partial pressure of the same hydrocarbon in the feed. This is the result of having deliberately set the flow rates to attain low transfer of hydrocarbons from feed to 15 sweep during testing. The total transfer of hydrocarbons from feed to sweep was kept at less than five percent the amount of hydrocarbons in the feed. It is preferable that this amount be less than one percent of the amount of hydrocarbons in the feed. Under these conditions, the partial pressure of hydrocarbons in the sweep were neglected in the calculation of permeance, and the permeances reported here were 20 calculated using the partial pressure of hydrocarbons in the feed as the total transmembrane pressure driving force.

It must also be pointed out that because of the low total transfer of hydrocarbons from feed to sweep, the partial pressure of hydrocarbons in the feed is constant across 25 the membrane surface. Because of this and the fact that the partial pressures of hydrocarbons in the sweep are negligible and uniform across the sweep side of the membrane, the partial pressure difference of each hydrocarbon across the membrane is constant across the entire membrane area. Therefore, the permeances reported here are considered point permeances to distinguish them from permeances one can 30 observe in large-area membranes where the concentrations in both feed and sweep sides are allowed to vary across the total membrane area (i.e., the transmembrane

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pressure difference varies across the membrane area). Such is the case of a large membrane module, where, if one applies the equation of permeance as written, the permeance obtained would be an average permeance in the membrane module. One may refer to this permeance as an integrated or module permeance which would be 5 different than the point permeances provided here. The importance of differentiating between a point permeance and an average or module permeance is that a point permeance is the parameter one must use in engineering the design of a membrane module. An average or module permeance, on the other hand, only applies to that specific membrane module under the testing conditions used.

10

The selectivity of a component A over a component B is calculated as follows:

$$\text{Selectivity A/B} = \frac{\text{Permeance of A}}{\text{Permeance of B}}$$

15

The selectivities and permeances for the layers are also provided in Table 1. Here it can be seen that the selectivity for paraxylene and the permeance for paraxylene of the layer manufactured according to the present invention is superior.

## 20 Characterization

SEM analysis after testing has shown that both layers show the same structure and thickness of the seed layer (0.5  $\mu\text{m}$ ), deposited molecular sieve layer (0.6  $\mu\text{m}$ ) and P1X reparation layer (1.1  $\mu\text{m}$ ). Under secondary electron imaging SEM, comparative 25 example 1 exhibits a dark zone of ca. 50  $\mu\text{m}$  thickness at the top of the support which is indicative of support invasion by material derived from the synthesis solution. This is confirmed by EDX analysis, element mapping and line scans for silicon. The layer according to the present invention does not show a dark zone and EDX shows very minor support invasion.

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The above process was repeated with a number of possible impregnating materials including silicone oils the results are provided in the following Table 2

Table 2: Impregnation Tests

5

Disk	Impregnation Method	Comments
Comparative Example 2	Soaking in silicon oil	Silicon oils escapes from support and floats on synthesis mixture. Part of disk surface is hydrophobic
Comparative Example 3	Soaking in hexadecane	Hexadecane escapes from support. SEM/EDX shows extensive support invasion
Comparative Example 4	Precipitation of $\text{CaCl}_2$ into pores of support	Almost completely inhibits zeolite layer growth
Comparative Example 5	Polyimide PIx 8144 deposition.	Forms overcoating. PIx layer comes off
Example 2	Soak in PVC dissolved in THF*** Applied to large pore support (80 to 160nm and larger) with no seed layer.	Minimal support invasion.
Example 3	Soak in molten H231 wax ( $T_m=110^\circ\text{C}$ ). Hydrothermal synthesis is at less than $110^\circ\text{C}$	Zeolite layer deposited no support invasion.

\*\* DTUP = di-iso-undecyl-phthalate

\*\*\* THF = terta-hydro-furan

10

Examples 4 to 12Preparation of Colloidal Seeds

15 Silicalite colloidal seeds of 50 nm particle size were prepared according to the general method described in WO93/08125.

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Spin Coating Seed Layer

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For spin-coating, a colloidal suspension of 0.5 % by weight of 50 nm sized MFI crystals with a pure silica composition was prepared according to the process of WO03/08125

10 A porous alpha-alumina disk, diameter 25 mm, thickness 3 mm, pore size 80 nm, 33% porosity, machined and polished on one face placed in the specimen chuck of a CONVAC Model MTS-4 spinner and brought up to a spinning speed of 4000 rpm. Once this spinning speed had been reached 2ml of the seed solution was applied to the centre of the disk and spinning was continued to a total of 30 seconds. The 15 coated disk was then removed from the spinner and placed in an oven and heated upto a temperature of 425°C or 450°C at a rate of 0.3°C/min and held at the terminal temperature for 6 hours. After 6 hours the coated disk was cooled at a rate of 0.5°C/min until the disk reached room temperature.

20 Impregnation

A petri dish was partially filled with H101 hydrocarbon wax which was melted at 150°C in a vacuum oven. The coated support was placed on a holder in the wax filled petri dish such that only the no-deposited surface of the support was submerged 25 in the wax. This ensured that the seed layer did not come into contact with the wax. The vacuum pump was switched on and after 2 minutes it was switched off at a vacuum of <50mbar. The oven was brought to atmospheric pressure and the impregnated wax was allowed to crystallise within the pores of the support. This impregnated support was now ready for deposition of an inorganic layer.

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Hydrothermal Synthesis Solutions

A solution was prepared of 0.92 g NaOH (98.4% purity) in 138.14 g of water. Into this solution was dissolved 7.12 g of tetrapropylammonium bromide (TPABr; 5 Fluka). To this mixture was added 76.66 g of colloidal silica solution (Ludox AS 40, supplied by Du Pont) and the resulting mixtures was stirred with a magnetic stirrer for 2 to 10 minutes. The resulting molar composition was as follows:

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0.22 Na<sub>2</sub>O: 0.52 TPABr: 10 SiO<sub>2</sub> :200 H<sub>2</sub>O

10

Hydrothermal Synthesis

The impregnated support with seed coating was mounted in a holder with the spin-coated face downwards, near the surface of the synthesis mixture in an autoclave. 15 The autoclave was closed, placed in an oven, and heated during 30 minutes to the crystallisation temperature and maintained at that temperature for the period specified in the following tables. The oven was then allowed to cool to room temperature. After cooling, the disk was removed and washed in demineralized water until the conductivity of the last washing water was  $\leq 5 \mu\text{S}/\text{cm}$ . The disk was then dried in an 20 oven at 125°C. After drying the resulting structure was calcined and tested for separations performance. The calcination conditions were sufficient to remove the impregnating material.

Further Coating Application

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A number of the molecular sieve layers were treated using the procedure described in Example 3 of WO96/01686 to provide a selectivity enhancing layer on the molecular sieve layer. The resulting structures were also tested for separations performance.

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Xylenes Separation Test

5 This was undertaken using the method identified above. The selectivity's permeances and permeability coefficients for the layers according to the present invention are provided in Table 3. The permeability coefficient for paraxylene is calculated by ~~dividing the permeance for paraxylene by the combined thickness of the seed and~~  
molecular sieve layers.

10

Examples 4 and 5 illustrate the effect of the additional step of reparation in the process of the present invention. Example 5 is reparated and exhibits exceptionally high selectivity for paraxylene whilst maintaining an acceptable permeance. The additional examples illustrate the good selectivities, permeances and permeability 15 coefficients observed with layers manufactured using the process of the present invention.

Helium Permeance and Weight Gain

20 A number of samples were prepared using the general procedure given above for Examples 4 to 12. The support was impregnated with hydrocarbon wax through the surface which was remote from the seed layer and to a depth of approximately 1mm from that surface. A further set of examples were prepared without support impregnation.

25

These samples were then evaluated to assess their permeance to Helium and to measure the weight gain of the support after deposition of the molecular sieve layer.

30 The results are provided in Figure 2. Figure 2 shows the inverse of helium permeance versus weight gain. The helium permeances in this figure are the values for the membrane only with correction for the support effects.

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The helium flow through the cleaned support is measured by pressurising one side of the support with helium at 2 bar absolute pressure whilst maintaining the opposite side at 1 bar absolute pressure. Helium flows from the high pressure side to the low pressure side where the flow (ml/min) is measured with the aid of a flow meter. The helium permeance in the support ( $Q_{He, Support}$ ) is then calculated by dividing the flow of helium measured by the product of the membrane area exposed to helium (in  $\text{cm}^2$ ) and the difference in pressure between the high and low pressure sides (1 bar).

5 The same procedure is performed after a membrane is grown on the support which gives the helium permeance in the membrane plus support ( $Q_{He, ZM+Support}$ ). By 10 using a series resistance model of the form:

$$1/Q_{He, ZM+Support} = 1/Q_{He, ZM} + 1/Q_{He, Support}$$

15 the helium permeance in the membrane only ( $Q_{He, ZM}$ ) is calculated.

It can be seen that those samples which were prepared in accordance with the invention exhibit a significantly higher helium permeance compared to the other samples and in addition exhibit significantly lower weight gains. The weight gain is 20 a combination of the desired inorganic layer and unwanted material which is deposited within the support structure

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Table 3

Example	SiO <sub>2</sub>	Temp	Time	pX <sub>y</sub> /mX <sub>y</sub> Selectivity, 6hrs	pX <sub>y</sub> Permeance, 6hrs	Seed Layer Thickness um	Molecular sieve layer thickness um	Combined Thickness um
1	20	90	36	3.2	53	0.5	0.5	
2	20	90	36	140	4.7	0.5	0.5	
3	20	90	36	2.8	53	0.5	0.5	
4	20	90	36	2.9	63.4	0.5	0.5	
5	20	90	36	2.1	88	0.5	0.5	
6	20	90	36	2.7	77	0.5	0.5	
7	20	90	36	3.2	85	0.5	0.5	
8	20	90	36	3.2	85	0.5	0.5	
9	20	90	36	6	90	0.5	0.5	

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CLAIMS:

1. A process for the manufacture of a supported inorganic layer, which process comprises:

5

a) providing a porous inorganic support which has at least one surface capable of receiving an inorganic layer,

10 b) impregnating the porous inorganic support through at least one surface thereof with a material capable of removal from the support after receipt of the inorganic layer and which material is not carbonised prior to receipt of the inorganic layer,

c) depositing or growing an inorganic layer on the surface mentioned in (a); and

d) substantially completely removing the impregnating material.

15

2. A process as claimed in claim 1 wherein the impregnating material is an organic resin.

20

3. A process as claimed in claim 2 wherein the organic resin is a hydrocarbon resin.

4. A process as claimed in claim 3 wherein the hydrocarbon resin is an acrylic resin.

25

5. A process as claimed in claim 3 wherein the hydrocarbon resin is a hydrocarbon wax.

6. A process as claimed in any of the preceding claims wherein the impregnating material substantially fills the pores of the support.

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7. A process as claimed in claim 1 wherein the surface capable of receiving an inorganic layer comprises a molecular sieve seed layer deposited thereon.
8. A process as claimed in claim 7 wherein the impregnating material substantially fills the pores of the seed layer and/or support.
9. A process as claimed in any of the preceding claims wherein the inorganic layer is a molecular sieve.

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10. A process as claimed in any one of the preceding claims wherein the porosity of the support is 30% by volume or greater.

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## ABSTRACT

### Processes for their Manufacture of Supported Materials

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A process is described for the manufacture of a support, which comprises impregnation of the support with an impregnating material prior to deposition of an inorganic layer and subsequent removal of substantially all the impregnating material.

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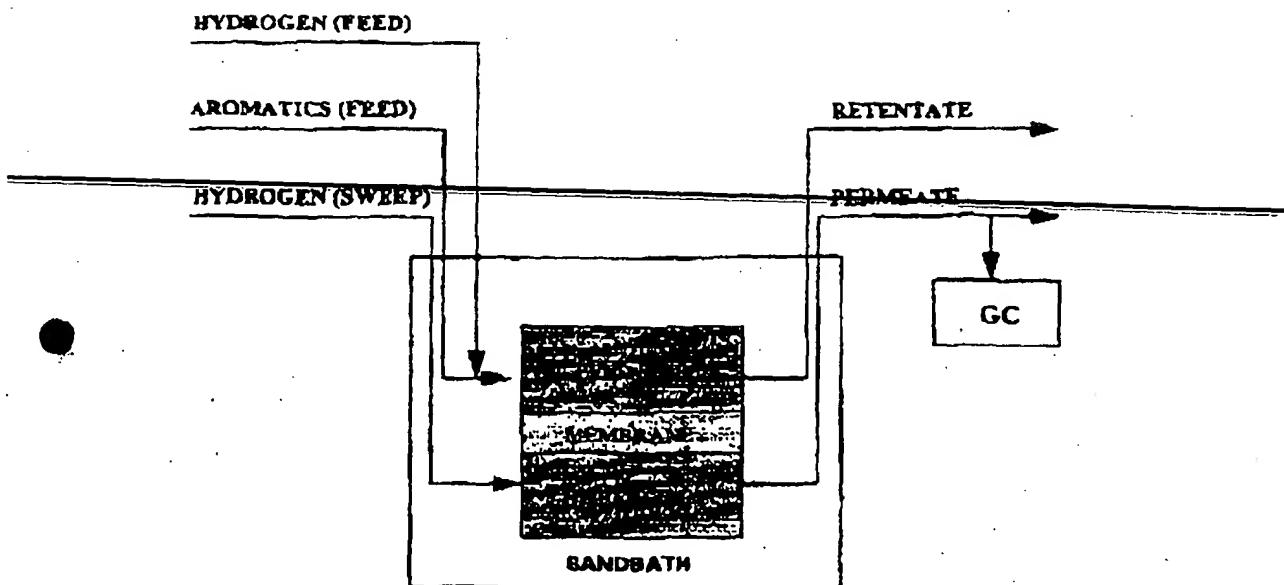
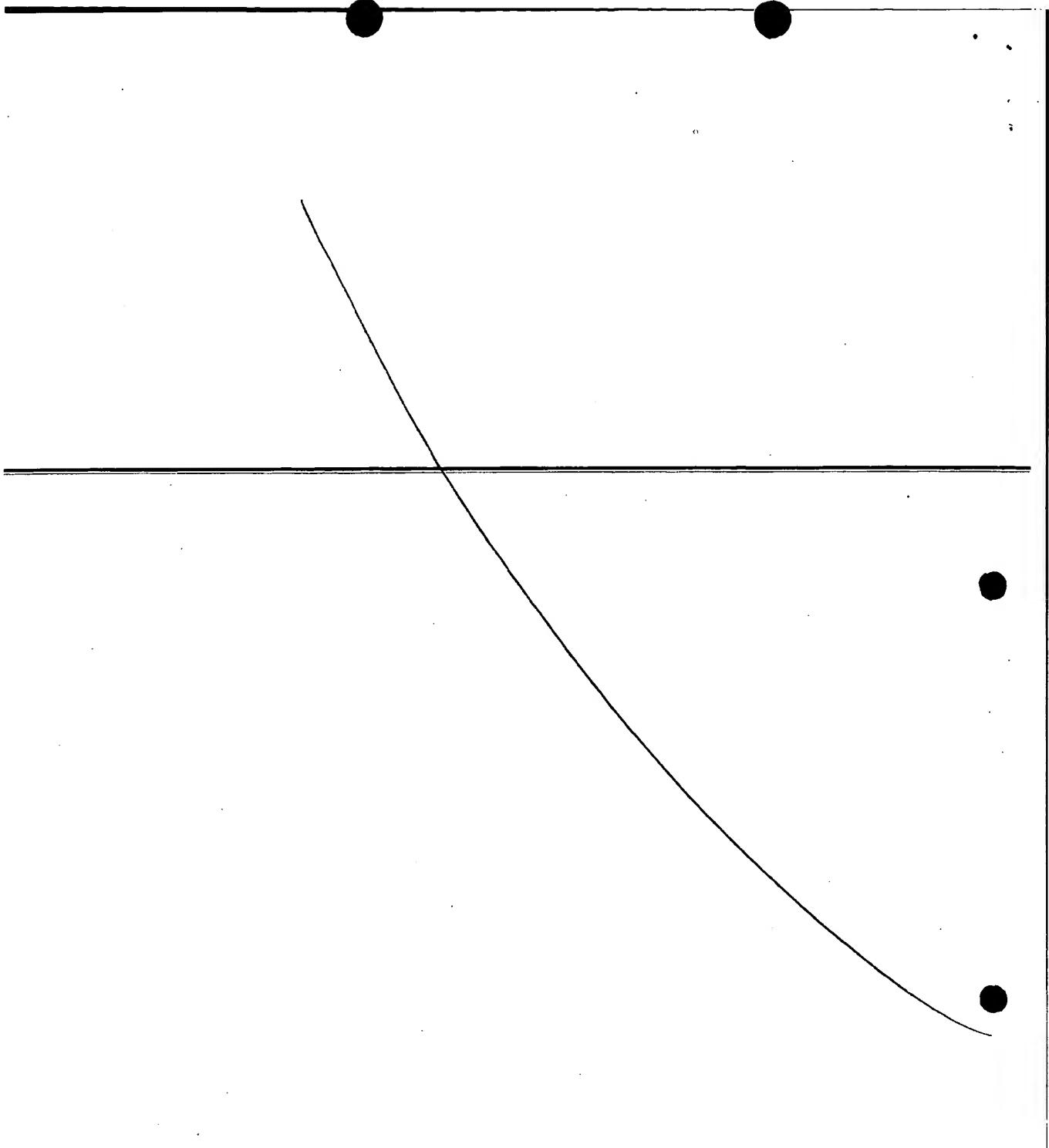


Figure 1: Simplified diagram of a unit used to test zeolite membranes.

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Figure 2.

